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(71) Applicant: **POLYPLASTICS CO. LTD.,**
30 Azuchimachi 2-chome, Higashi-ku Osaka-shi (JP)

(72) Inventor: **Takahashi, Katsuhiko, 324, Miyashita, Fuji-shi Shizuoka (JP)**
Inventor: **Nakashima, Tuneyasu, 5-18-22-304, Arima Miyamae-ku, Kawasaki-shi Kanagawa (JP)**

(74) Representative: **Livsey, Gilbert Charlesworth Norris et al, HYDE, HEIDE & O'DONNELL 146 Buckingham Palace Road, London SW1W 9TR (GB)**

(54) **Polyester composition having superior resistance to hot water.**

(57) A polyalkylene terephthalate resin composition comprises a polyalkylene terephthalate resin,
(A) at least one selected from the group consisting of ethylene/alkyl acrylate and a thermoplastic polyester elastomer and
(B) at least one selected from the group consisting of an epoxy resin containing at least two epoxy groups in the molecule and a polycarbodiimide containing at least two carbodiimide groups in the molecule.

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POLYESTER COMPOSITION HAVING SUPERIOR RESISTANCE TO HOT WATER

The present invention relates to a polyalkylene terephthalate resin composition having superior resistance to hot water suitably used in warm or hot water or in an atmosphere of steam.

Polyalkylene terephthalate resins have been widely used in various fields of industry as engineering plastics superior in mechanical and physical properties. Heretofore, a large number of polyalkylene terephthalate resin compositions having improved characteristics according to the properties required in these various fields of industry have been proposed. The present applicant provides herein a polyalkylene terephthalate resin composition having superior resistance to hot water as one of such polyalkylene terephthalate resin compositions. Although polyalkylene terephthalate resins are resistant to hot water to some degree per se, the application of these resins in car parts, which must be used in an atmosphere of hot water, has a problem that they are hydrolyzed after a considerably short time, thereby suffering deterioration in physical properties, in particular, tensile strength and elongation. Although the addition of phosphorus compounds, diene compounds, oxetane compounds or mixtures thereof to the polyalkylene terephthalate resins has been proposed in order to solve

such a problem, no satisfactory solution has been reached as yet. The present inventors have repeated investigations for solving such a problem by imparting hydrophobicity to the resin and simultaneously forming some network structures in the resin. The present invention was completed on the basis of these investigations and it relates to a polyalkylene terephthalate resin composition having superior resistance to hot water, characterized by comprising a polyalkylene terephthalate resin, to which are added (A) at least one selected from the group consisting of ethylene/alkyl acrylate and thermoplastic polyester elastomer and (B) at least one selected from the group consisting of an epoxy resin and a polycarbodiimide, each in a desired amount.

As is well known, the polyalkylene terephthalate resin used in the present invention is a polyester obtained by the polycondensation between terephthalic acid or its lower alkyl ester and a alkylenediol. For example, a polybutylene terephthalate resin, which is produced by an ester-exchange reaction and subsequent polycondensation between dimethyl terephthalate and 1,4-butanediol, are most suitable for the base resin in the present invention. Also copolymers containing polybutylene terephthalate as the main ingredient or mixtures thereof with polyethylene terephthalate and the like may be used. In addition, it is desirable in the present invention that the polyalkylene terephthalate resin contains glass fibers in an amount of 0 to 60% by weight therein.

According to the present invention, at least one selected from the group consisting of ethylene/alkyl acrylate and a thermoplastic polyester elastomer, as the ingredient (A), is added to the polyalkylene terephthalate resin in an amount of 1 to 50% by weight based on the total resin composition. If it is added in an amount smaller than that, no sufficient effect can be reached, while if it is added in an amount larger

than that, the strength of the resin is deteriorated. Thus it is most preferably added in an amount of 3 to 25% by weight. The ingredient (A) serves to impart elasticity to the resin and is particularly effective in improving impact resistance and elongation. However, the addition of it alone to the polyalkylene terephthalate resin can bring about no appreciable improvement in the resistance to hot water. The effect of improving the resistance to hot water, or, to hydrolysis can be remarkably increased by using these substances together with additives comprising ingredient (B). The ethylene/alkyl acrylate herein refers to a copolymer consisting of ethylene and an alkyl acrylate in an arbitrary ratio, among which an ethylene/ethyl acrylate copolymer is the most useful. The thermoplastic polyester elastomers are preferably segmented copolyesters consisting of repeating long-chain units and short-chain units. The ingredient (B), that is, at least one selected from the group consisting of an epoxy resin and a polycarbodiimide is added to the polyalkylene terephthalate resin in addition to the ingredient (A), that is, ethylene/alkyl acrylate or a thermoplastic polyester elastomer in the production of the composition according to the present invention. The ingredient (B) is added in an amount of 0.1 to 10% by weight based on the total resin composition. The addition thereof in an amount smaller than that is ineffective in improving to resistance to hot water by establishing a three-dimensional, or a network structure in the resin, while the addition of a too large amount thereof lowers the fluidity of the resin. Therefore, it is preferably added in an amount of 0.5 to 5% by weight. Although it is effective in improving the resistance to hydrolysis even when added by itself, a remarkable improvement in the resistance to hot water was observed by adding it together with the ingredient (A), that is, anyone of the ethylene/alkyl acrylate and the thermoplastic polyester

elastomer. The epoxy resins used in the present invention are diepoxide compounds containing at least two epoxy groups in the molecule and produced by the known methods and include polycondensates between an epihalohydrin such as epichlorhydrin and a diol preferably containing up to 15 carbon atoms, such as diphenylolpropane (hereinafter referred to as diphenol "A"), in an arbitrary ratio; bis (2, 3-epoxypropanol) esters obtained by an esterification reaction between a dicarboxylic acid preferably containing up to 15 carbon atoms, such as terephthalic, phthalic, 2,6-naphthalene dicarboxylic, adipic, succinic or dodecane dicarboxylic acid, and 2,3-epoxypropanol; and cycloaliphatic diepoxides preferably containing 5 to 15 carbon atoms, such as cyclooctadiene-(1,5) diepoxide, 1,2,5,6-diepoxycyclododecane-(9), bicycloheptadiene diepoxide or dicyclopentadiene diepoxide.

The polycarbodiimides are compounds containing at least two carbodiimide groups in the molecule, which are usually derived from isocyanate compounds. Preferred carbodiimide compounds include those derived from aromatic diisocyanates such as phenylene diisocyanate, toluene diisocyanate, methylenebisphenyl diisocyanate and xylene diisocyanate and aliphatic diisocyanates such as hexamethylene diisocyanate and isophorone diisocyanate.

Further, known additives, for example, various kinds of stabilizer, lubricant, nucleating agent, plasticizer, releasing agent, antistatic agent, flame resisting agent, organic high-molecular material for improving physical properties, fibrous, acicular, plate-like or powdery inorganic substances or metals, or colouring agents such as carbon black and other dyes and pigments may be suitably added to the composition according to the present invention, if necessary.

The composition according to the present invention may be obtained in the form of pellet by extruding the compound, which was prepared by blending a mixture

consisting of a polyalkylene terephthalate resin and given amounts of necessary additives added to said polyalkylene terephthalate resin at once in a blender, an extruder, or by extruding in at least two steps, for example, extruding the compound containing part of said necessary additives and then adding the rest of the necessary additives followed by extruding the resulting compound again. In addition, some kinds of ingredient may be added in the molding process in order to obtain molded products containing them.

The obtained pellets of the composition are preliminarily dried and then molded to obtain molded products comprising a polybutylene terephthalate composition having superior resistance to hot water.

The present invention will now be described in more detail with reference to the examples. It should, however, be understood that the present invention is by no means limited to these examples. All of the amounts of ingredients described in examples and comparative examples are represented in % by weight.

Examples 1 to 12

Given amounts of substances A and B as shown in Table 1 are added to a polybutylene terephthalate resin (PBT) containing glass fibers in an amount of 30%. The resulting mixture is blended in a blender and then extruded in an extruder to prepare pellets. The resulting pellets are dried in an atmosphere of hot air all night and then molded in a molding machine to prepare test pieces. The test pieces, which were dipped in hot water of 95°C for given periods, were tested on tensile strength in order to study changes in the tensile strength with time. These tests were carried out in accordance with ASTM D638-58T on a Toyo-Baldwin tension tester UTM-1-2500. The results are shown in Table 1.

Comparative Examples 1 to 6

The test pieces are prepared in the same manner as in Examples except that both or either of said substances A and B are not added. The tests were carried out under the same conditions as in Examples. The results are shown in Table 1.

As to numerical values described in Table 1, those in the upper columns indicate the tensile strength (kg/cm^2), those in the lower columns indicating the elongation (%), and those in parentheses indicating the retaining rate when the initial value is 1.00.

As understood from the results obtained in Examples and Comparative Examples, the composition according to the present invention can remarkably prolong the service life of resins for the uses requiring resistance to hot water and hold superior values of tensile strength and elongation even in an atmosphere of warm or hot water. Therefore, the present invention can provide a polybutylene terephthalate resin composition remarkably suitable for use in the presence of water, in particular, at higher temperatures, for example, for use as car parts.

Table 1

			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Composition (% by weight)	PBT containing 30% glass fibers		95.2	89.2	79.2	95.2	88	94	95.2	89.2	79.2	95.2	88	94
	Substance A		*1 4	*1 10	*1 20	*2 4	*1 10	*2 4	*1 4	*1 10	*1 20	*2 4	*1 10	*2 4
	Substance B		*3 0.8	*3 0.8	*3 0.8	*3 0.8	*3 2	*3 2	*4 0.8	*4 0.8	*4 0.8	*4 0.8	*4 2	*4 2
	Others		-	-	-	-	-	-	-	-	-	-	-	-
Number of days during which the test pieces are dipped	0 day	Tensile strength	1229 (1.00)	1175 (1.00)	1081 (1.00)	1233 (1.00)	1102 (1.00)	1263 (1.00)	1251 (1.00)	1180 (1.00)	993 (1.00)	1241 (1.00)	1192 (1.00)	1302 (1.00)
		Elongation	3.0 (1.00)	3.3 (1.00)	3.5 (1.00)	3.1 (1.00)	3.4 (1.00)	3.1 (1.00)	3.0 (1.00)	3.3 (1.00)	4.1 (1.00)	3.1 (1.00)	3.2 (1.00)	2.9 (1.00)
	5 days	Tensile strength	1131 (0.92)	1093 (0.93)	973 (0.90)	1147 (0.93)	1123 (0.95)	1187 (0.94)	1151 (0.92)	1086 (0.92)	884 (0.89)	1142 (0.92)	1120 (0.94)	1210 (0.93)
		Elongation	2.6 (0.80)	2.9 (0.87)	3.1 (0.89)	2.6 (0.84)	3.0 (0.89)	2.6 (0.85)	2.7 (0.89)	2.9 (0.88)	3.6 (0.88)	2.6 (0.85)	2.9 (0.90)	2.4 (0.83)
	10 days	Tensile strength	1106 (0.90)	1034 (0.88)	886 (0.82)	1048 (0.85)	1076 (0.91)	1086 (0.86)	1101 (0.81)	1027 (0.87)	794 (0.80)	1067 (0.86)	1073 (0.90)	1146 (0.88)
		Elongation	2.5 (0.83)	2.7 (0.83)	3.0 (0.85)	2.3 (0.73)	2.9 (0.84)	2.4 (0.78)	2.5 (0.84)	2.7 (0.82)	3.6 (0.87)	2.5 (0.80)	2.8 (0.86)	2.2 (0.77)
	15 days	Tensile strength	1069 (0.87)	1011 (0.86)	865 (0.80)	1011 (0.82)	1040 (0.88)	1048 (0.83)	1038 (0.83)	991 (0.84)	725 (0.73)	1042 (0.84)	930 (0.78)	1107 (0.85)
		Elongation	2.1 (0.70)	2.4 (0.72)	2.6 (0.75)	2.1 (0.67)	2.5 (0.73)	2.1 (0.69)	2.0 (0.69)	2.3 (0.70)	3.2 (0.77)	2.1 (0.68)	2.3 (0.73)	1.9 (0.64)
	20 days	Tensile strength	922 (0.75)	881 (0.75)	767 (0.71)	900 (0.73)	890 (0.76)	960 (0.76)	888 (0.71)	885 (0.75)	636 (0.64)	931 (0.75)	810 (0.68)	1042 (0.80)
		Elongation	1.8 (0.60)	2.1 (0.65)	2.3 (0.66)	1.8 (0.59)	2.0 (0.59)	1.7 (0.55)	1.8 (0.60)	2.0 (0.61)	2.8 (0.68)	1.8 (0.57)	2.0 (0.61)	1.5 (0.52)
	30 days	Tensile strength	676 (0.55)	682 (0.58)	551 (0.51)	641 (0.52)	745 (0.63)	758 (0.60)	625 (0.50)	637 (0.54)	417 (0.42)	558 (0.45)	668 (0.56)	664 (0.51)
		Elongation	1.3 (0.43)	1.6 (0.47)	1.8 (0.50)	1.4 (0.45)	1.5 (0.44)	1.3 (0.41)	1.35 (0.45)	1.6 (0.47)	2.2 (0.54)	1.3 (0.43)	1.5 (0.48)	1.1 (0.37)

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			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Composition (% by weight)	PBT containing 30% glass fibers		100	90	89.5	96	90	98
	Substance A		-	*1 10	*1 10	*2 4	-	-
	Substance B		-	-	-	-	*3 2	*4 2
	Others		-	-	*5 0.5	-	-	-
Number of days during which the test pieces are dipped	0 day	Tensile strength	1376 (1.00)	1100 (1.00)	1170 (1.00)	1290 (1.00)	1350 (1.00)	1367 (1.00)
		Elongation	2.8 (1.00)	2.9 (1.00)	2.8 (1.00)	2.8 (1.00)	2.8 (1.00)	2.8 (1.00)
	5 days	Tensile strength	1220 (0.82)	1030 (0.88)	550 (0.47)	1053 (0.82)	1161 (0.86)	1217 (0.89)
		Elongation	2.2 (0.77)	2.3 (0.79)	0.9 (0.31)	2.0 (0.77)	2.2 (0.77)	2.3 (0.81)
	10 days	Tensile strength	936 (0.68)	850 (0.72)	363 (0.31)	764 (0.59)	906 (0.76)	1025 (0.75)
		Elongation	1.5 (0.52)	1.6 (0.54)	0.6 (0.23)	1.2 (0.46)	1.9 (0.69)	0.8 (0.76)
	15 days	Tensile strength	743 (0.54)	578 (0.49)	257 (0.22)	573 (0.44)	904 (0.67)	875 (0.64)
		Elongation	1.0 (0.36)	1.1 (0.39)	0.5 (0.18)	0.8 (0.31)	1.7 (0.60)	1.4 (0.51)
	20 days	Tensile strength	481 (0.35)	-	-	-	-	-
		Elongation	0.8 (0.29)	-	-	-	-	-
	30 days	Tensile strength	358 (0.26)	-	-	-	-	-
		Elongation	0.5 (0.18)	-	-	-	-	-

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(Notes) *1: Ethylene/ethyl acrylate (EEA-BRT-490, a product of Nihon Unicar Co. Ltd.)

*2: Polyester elastomer (Hytrel-4056, a product of Showa Neoprene Co. Ltd)

*3: Polycarbodiimide (Stavakzol-PCD, a product of Hiraizumi Yoko Co. Ltd)

*4: Epoxy resin (Epikote 819, a product of Toray Industries, Inc.)

*5: Tridecyl phosphite

CLAIMS

1. A polyalkylene terephthalate resin composition which comprises a polyalkylene terephthalate resin,

(A) at least one selected from the group consisting of ethylene/aklyl acrylate and a thermoplastic polyester elastomer and

(B) at least one selected from the group consisting of an epoxy resin containing at least two epoxy groups in the molecule and a polycarbodiimide containing at least two carbodiimide groups in the molecule.

2. A composition as set forth in Claim 1, wherein said polyalkylene terephthalate resin contains glass fibers in an amount of 0 to 60% by weight therein.

3. A composition as set forth in Claim 1 or 2, wherein said ethylene/alkyl acrylate or thermoplastic polyester elastomer is added in an amount of 1 to 50% by weight based on the total composition.

4. A composition as set forth in Claim 1 or 2, wherein said epoxy resin or polycarbodiimide is added in an amount of 0.1 to 10% by weight based on the total composition.

5. A composition as set forth in any of Claims 1 to 4, wherein said polyalkylene terephthalate resin comprises polybutylene terephthalate as the main ingredient.

6. A composition as set forth in any of Claims 1 to 5, wherein said ethylene/alkyl acrylate comprises ethylene/ethyl acrylate.